

DESULPHURIZATION OF MODEL OIL AND DIESEL USING IONIC LIQUID

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**Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)**

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

27 JANUARY 2014

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ABSTRACT

Diesel is a multi-purpose petroleum fuel used in all kinds of vehicles. But remains one of the largest source of fine particle air pollution, which has serious health impacts. Depending on the crude oil used and the refinery configurations, sulphur levels in diesel range from below 10 ppm to as high as 1000 ppm. In fact, Europe, United States, and Japan have all put in place measures to reduce sulphur to lower levels which is below 10 ppm to 15 ppm, often along with emission standards that require advanced emission control technologies that cannot be used with higher sulphur fuels. By March of 2008, there are many countries that have switched to diesel fuel with 500 ppm or less such as Philippines, Singapore, and Thailand including our country, Malaysia. There are various methods applied in industry to obtain low-sulphur fuels such as hydrocracking processes. But, the sulphur removal using ionic liquids are gaining wide recognition as potential environmental solvents due to their very low vapour pressure, their thermal and chemical stability, their ability to act as a catalyst, and their non-flammability and non-corrosive properties. The procedures include with three sub-process which first (ILs) is analyse with Fourier transform infrared spectroscopy (FTIR). The liquid was placed on a Germanium (Ge) plate by using a dropper and the test is run until a constant reading is visible. It is then followed by a wavelength classification by referring it to a table of characteristic IR absorptions. From the classification, it was found that there is a trace of functional groups consists of amines, amides, aromatics and alkyl halides. The lower frequency, 874.55 cm^{-1} and 777.29 cm^{-1} have functional group of aromatics with bond C-H "oop". The highest frequency with 3421.96 cm^{-1} has functional group of 1° , 2° amines or amides with bond N-H Stretch. Besides, there are also components with functional group of aliphatic amines with bond C-N Stretch at frequency 1044.97 cm^{-1} and 1104.56 cm^{-1} respectively. Other than that, there is functional group of alkyl halides with bond C-H wag (CH_2X) at frequency 1179.15 cm^{-1} . Secondly, the ionic liquid was undergone a CHNOS testing to check the percentage of carbon (C), Nitrogen (N), Oxygen (O), and Sulphur (S) that presented within ionic liquids. The ionic liquid was sent to University Malaysia Pahang (UMP) Central Laboratory to obtain the results. Based on the result obtained, the (ILs) consists of Nitrogen by 11.37%, Carbon by 15.84%, Hydrogen by 6.729%, Sulphur by 11.185% and rest of the composition is for Oxygen by 15.84%. The result will be compared theoretically with the structure formula of (ILs).

ABSTRAK

Diesel adalah bahan api petroleum pelbagai guna yang digunakan dalam semua jenis kenderaan. Tetapi ianya juga menjadi salah satu sumber terbesar pencemaran udara zarah halus, yang mempunyai kesan kesihatan yang serius. Bergantung kepada minyak mentah yang digunakan dan konfigurasi penapisan, sulfur dalam julat diesel dari bawah 10 ppm kepada setinggi 1000 ppm. Malah, Eropah, Amerika Syarikat, dan Jepun telah semua melaksanakan langkah-langkah untuk mengurangkan sulfur ke tahap yang lebih rendah iaitu di bawah 10 ppm hingga 15 ppm, sering bersama-sama dengan standard pelepasan yang memerlukan kemajuan teknologi dalam kawalan pelepasan yang tidak boleh digunakan dengan bahan api sulfur yang lebih tinggi. Menjelang Mac 2008, terdapat banyak Negara yang telah bertukar kepada bahan api diesel dengan 500 ppm atau kurang seperti di Negara Filipina, Singapura dan Thailand termasuk juga Negara kita, Malaysia. Terdapat pelbagai kaedah yang digunakan dalam industri untuk mendapatkan bahan api rendah sulfur seperti proses pemecahan hidro. Tetapi, penyingkiran sulfur menggunakan cecair ionic semakin mendapat sambutan yang meluas sebagai pelarut yang mesra alam sekitar disebabkan oleh tekanan wap yang sangat rendah, kestabilan haba dan kimia mereka, keupayaan mereka untuk bertindak sebagai pemangkin dan sifat-sifat tidak mudah terbakar dan tidak cepat mengakis mereka. Prosedur ini termasuk dengan tiga sub-proses yang pertama adalah menganalisis cecair ionic (ILs) dengan Spektroskopi (FTIR). Cecair tersebut telah diletakkan pada satu Germanium (Ge) plat dengan menggunakan penitis dan ujian dijalankan sehingga bacaan berterusan boleh dilihat. Ia kemudian diikuti dengan klasifikasi panjang gelombang dengan merujuk kepada jadual absorptions IR. Dari klasifikasi, didapati bahawa terdapat kesan kumpulan berfungsi mengandungi amina, amides, aromatic dan alkil halida. Kedua, cecair ionic akan menjalani ujian CHNOS untuk memeriksa peratusan Karbon (C), Nitrogen (N), Oksigen (O), dan Sulfur (S) yang dibentangkan dalam cecair ionic. Cecair ionic telah dihantar ke Makmal Pusat Universiti Malaysia Pahang (UMP) untuk mendapatkan keputusan. Berdasarkan keputusan yang diperolehi, (ILs) terdiri daripada Nitrogen oleh sebanyak 11.37%, Karbon sebanyak 15.84%, Hidrogen sebanyak 6.729% dan Sulfur sebanyak 11.185% dan selebihnya daripada komposisi Oksigen dengan 15.84%. Hasilnya akan dibandingkan secara teori dengan formula struktur daripada (ILs).

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LIST OF ABBREVIATIONS

DPF	Diesel particulate filter
ILs	Ionic liquids
EPA	Environmental protection agency
ULSD	Ultra-low sulfur diesel
HDS	Hydrodesulfurization
BDS	Biodesulfurization
ODS	Oxidative desulfurization
ADS	Adsorptive desulfurization
ppm	Part per millions
NMR	Nuclear magnetic resonance spectroscopy
FIA	Fluorescent indicator analysis
GC	Gas chromatography
SCTMAT	Short contact time microactivity test unit
FCC	Fluid catalytic cracking
DBT	Dibenzothiophene
BMIM	n-butyl-n-methylimidazolium
HPLC	High Performance Liquid Chromatograph
FTIR	Fourier Transforms Infrared Spectroscopy

1 INTRODUCTION

1.1 Motivation and statement of problem

Sulphur content in fuel has become a major environmental issue worldwide. Since June of 2006, the regulations in the US have required a reduction of sulphur in transport fuel from 500 ppm to 15 ppm. Meanwhile, in Europe, the regulation on sulphur in transport fuel required it to be less than 10 ppm by 2010. In addition, there are different form of compounds within sulphur which present in diesel which about 70% are made up by thiophene and its derivatives. The sulphur content in diesel is in the range of 0.1% to 10% depending on a place of origin. The sulphur content increases as the temperature of boiling point of individual fractions increases. The most sulphur which is about 98% contained in diesel fuel is oxidized in the combustion process to sulphur dioxide which together with exhaust gas is released to the atmosphere where it can be subject to other reactions contributing to the creation of smog and acid rains. Until now, desulphurization can only be obtained via heterogeneous catalytic hydrodesulphurization (HDS) process in petroleum plants. The main drawbacks of the (HDS) process include high operating temperature of 300 °C or more, high pressure of up to 4 MPa, high energy costs and difficulty in removing aromatics heterocyclic sulphur components such as benzothiophene (BT) and its derivatives. Therefore, ionic liquids (ILs) may be potential candidates in overcoming (HDS) drawbacks in removing heterocyclic sulphur components (Syamsul et al. 2011).

In the present study, the physical property of 1-Methylpyrazolium Methylsulphate has been highlighted to gain more efficiency for desulphurization process. By using statistical approach and manipulating the data, a comparison and explanation for the physical properties of the (ILs) in the plotted data could help predict the desulphurization performance for a new emerging (ILs).

1.2 Objective

The following are the objective of this research:

- To characterize the ionic liquid, 1-Methylpyrazolium Methylsulphate

- To study the extraction process for the removal of sulphur containing compound, DBT from model oil by means of an ionic liquid.

1.3 Scopes of this research

The following are the scope of this research:

- i) Study the characterization of 1-Methylpyrazolium Methylsulphate by their molecular structure and functional groups.
- ii) Evaluate the performance of 1-Methylpyrazolium Methylsulphate on model oil (DBT + xylene).
- iii) Test the extraction process on diesel with 1-Methylpyrazolium Methylsulphate.

1.4 Main contribution of this work

The following are the contributions of this research.

Firstly, the research will give the complete informations to the people about the effect of the sulphur content in diesel when release to the environment during combustion process. Sulphur release to the environment will lead to many serious problems such as the formation of acid rain that harmful to the human being and others living things.

Secondly, at the end of this research, the new diesels (after desulfurization process) definitely will reduce the sulphur content from the pure diesel in a certain amount. The diesel now is becoming cleaner without giving any single effect on it performance in the automobile's engines.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides general information about the diesel properties and characteristic. The information also includes the sulphur containing compounds in diesel and the effect of sulphur containing compounds release to the environment when reacts in combustion process. Besides, this chapter also review on the status of fuel quality on Asia pacific region and their target level of sulphur content in diesel for many years to come. The lower sulphur content in diesel will achieve the clean fuel status which is demanding by

the global associations. This chapter also explains about what are the ionic liquids and its properties which attract worldwide industries attention to use it as an extractants in the desulfurization process. It also includes the ionic liquids set for my later experiments on desulfurization of model oil and diesel. Lastly, the summary on the previous experiment set up by the others in their journals and articles on desulfurization process by using various types of ionic liquids on various type of model oil or fuel.

Chapter 3 gives a review of the chemicals and the apparatus needed to set up the experiment. There are several chemicals that we need to purchase it from the supplier such as ionic liquids, xylene, DBT and Methanol because it will not be supply by the University's laboratory. In addition, the apparatus such as thermometer, test tube, magnetic stirrer and the rest are mostly available from the laboratory. Then, this chapter explains about the methodology. The methodology divides into three parts which are preparation of ionic liquids, extraction on model oil and lastly, it will be the extraction on diesel.

Chapter 4 is supposed to be the extraction on model oil with ionic liquid. The experiment is set up by preparing the model oil with DBT and xylene to give certain volume of the solutions with sulphur content. The expected result from this experiment is the selected ionic liquid 1-Methypyrazolium Methylsulphate be able to remove the sulphur content, DBT from the model oil and the early aim for utmost objective is achieve.

Chapter 6 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

2 LITERATURE REVIEW

2.1 Introduction

This paper presents the experimental studies on desulfurization of diesel and model oil by using ionic liquids. Firstly, the preferred ionic liquids must be able to use as an extractant for desulfurization of model oil before it will be tested with diesel. The good extractant will exhibit a better extractive performance for removal of selected sulphur compounds. The ionic liquid is prepared and tested on model oil. Then, the ionic liquid is tested on diesel to compare the results.

2.2 Overview of Diesel

Diesel is a complex mixture of hydrocarbons with a boiling range from about 400 to 670°F. Besides that, it is also composed of hydrocarbons of three major classes: paraffinic, naphthenic, and aromatic hydrocarbons. In an analysis of diesel done by some researcher, the biggest setback is the separation and identification of pure compounds or classes of compounds from the complex hydrocarbon mixtures in diesel. The analysis uses the fluorescent indicator analysis method (FIA; ASTM D-1319) to separate and quantify saturates, olefins and aromatic hydrocarbons in diesel fuels. Another approach is to determine aromatic content by nuclear magnetic resonance spectroscopy, (NMR). These methods do not give the same result because they do not measure the same properties (Thomas, et al. 1991).

On the other hand, in a work presented by a number of researchers which was to determine sulphur compounds in diesel using Gas Chromatography (GC). In this work, it was known that a mixture of standard substances containing thiols, sulphides, thiophenes, benzothiophenes, dibenzothiophenes and benzonaphthothiophenes was present in diesel. Besides that, by using a one-dimensional chromatography it requires a very high column efficiency and stability in retention time of substances to avoid errors of the identification. On the flipside, by using a two-dimensional chromatography it is easier and more reliable to be identified due to the substance can be determined by both X- and Y-axis (Wei et al. 2003).

Furthermore, a study done by a researcher on the removal of thiophene sulphide from diesel. In this research, the researchers agreed that the sulphur in the fuels are hazardous, which not only pollute environment but also corrode equipment. Therefore, sulphur removal from fuels becomes an increasing technical challenge in refinery industry. On top of that, the difficulty of sulphides removal is closed related to the sorts of sulphides. The active sulphides such as hydrogen sulphide and thiols are easy to remove, but nor to the inactive sulphides with aromatic rings such as thiophene and its derivatives (Xin and Yong, 2005).

Table 2-1: Status of Fuel Quality on Asia-Pacific Region

Country	Sulphur (Max, ppm), Diesel	50 ppm Target Date
China	2,000	2016
India	500	No Date
Indonesia	3,500	No date
Malaysia	500	2016
Philippines	500	2010
Republic of Korea	50	2012
Singapore	50	2012
Thailand	500	2012
Vietnam	500	2016

Table 1 shows the sulphur content emission for selected Asia-Pacific country. It is known that some of the country has reached its target of 50 ppm of sulphur content for diesel emission. The European Standard has named this target as Euro IV.

Table 2-2: Analysis of Sulphurs-Containing Compounds of Diesel Samples (Wang et al., 2003).

Name	7000 ppm	1200 ppm	120 ppm
MST	1099	19	0
BT	0	0	0
C1BT	9	0	0
C2BT	88	3	0
C3BT	391	17	0
C4BT	477	24	0
C5BT	468	29	0
C6BT	457	35	0
C7BT	470	41	0
C8BT	457	44	0
C9BT	364	43	0
C10BT	328	41	0
C11BT	247	33	0
C11+BT	152	25	0
C0DBT	83	7	1
C1DBT	306	91	3
C2DBT	503	234	23
C3DBT	484	250	34

C4DBT	315	156	23
C5DBT	222	103	16
C6+DBT	164	81	12
Total	7085	1277	111

From Table 2, it is clearly stated that the sulphur compounds in diesel have different kind of various form and structure. From this research perspective, it is important to test an ionic liquid whether it is capable to remove or extract sulphur from diesel by evaluate it first on a model oil xylene which containing DBT as sulphur containing compound. By testing it on the model oil, it is to determine the effectiveness of the removal of sulphur before conducting it on diesel.

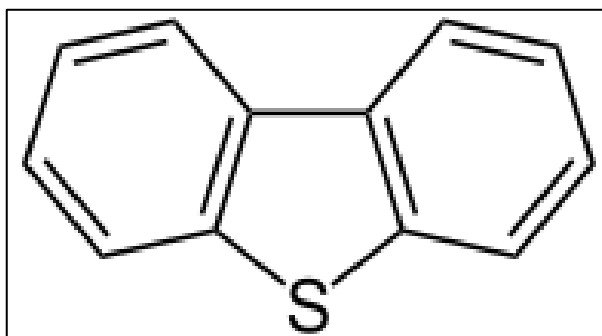


Figure 2-1: The structure of selective sulphur component in diesel DBT.

Table 2-3: The properties of the selective sulphur component in diesel DBT.

Solubility in water	Insoluble in water
Molar mass	184.26 g/mol
Appearance	Colourless crystals

Boiling point	323-333 °C(lit.)
Melting point	97-100 °C(lit.)
Density	1.252 g/mL at 25 °C(lit.)

2.3 Ionic Liquids

The Room temperature ionic liquids (RTIL) are liquids that are composed entirely of ions. In fact, ionic liquids can now be produced which remain liquid at room temperature and below (even as low as -90 °C) and appear to be undemanding and inexpensive to manufacture. Ionic liquids offer an attractive alternative to conventional organic liquids for clean synthesis, as they are easy to recycle, lack flammability, and effectively possess no vapour pressure. Compared with classical molecular solvents, the ionic liquids are environmentally benign reaction media (Hou^a, R. S. et al., 2006).

The 1-Methylpyrazolium Methylsulphate is one of the example (RTIL) which is known as a viscous, colourless, and hydrophobic and non-water soluble ionic liquids. It has a capability to absorb a little amount for paraffins and olefins, but absorbed a small amount of aromatics and a larger amount of thiophene and methylthiophene.

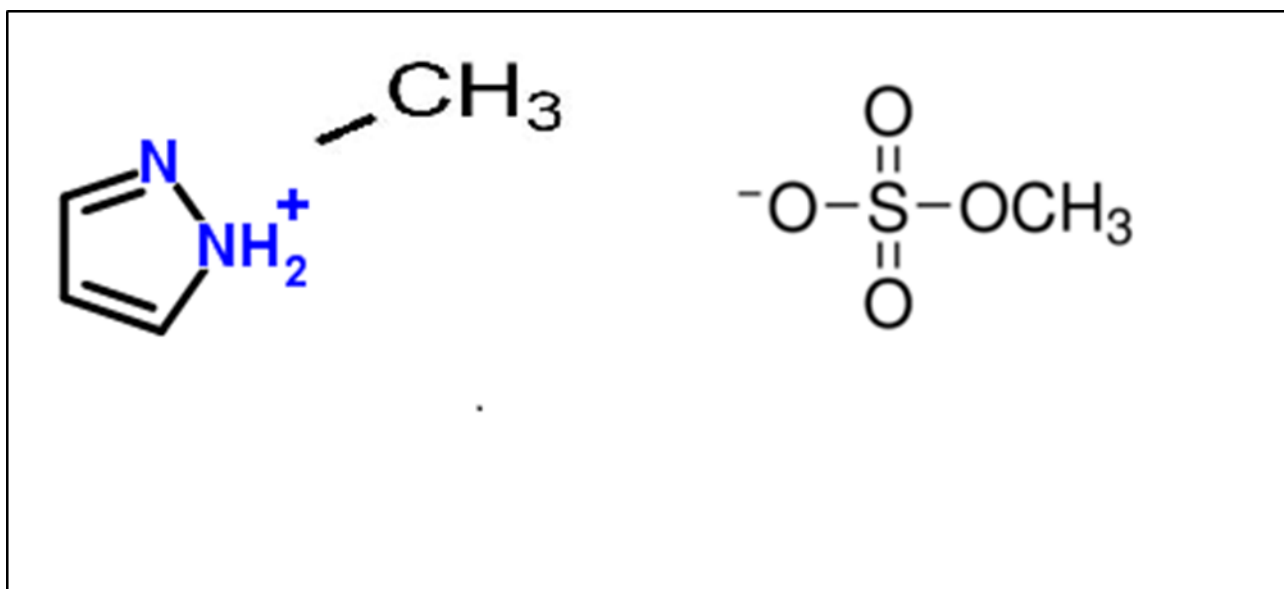


Figure 2-2: The structure of selected ionic liquid 1-Methylpyrazolium Methylsulphate

2.4 Usage of Ionic Liquids

The following chart summarizes important properties of ionic liquids and their potential with current applications:

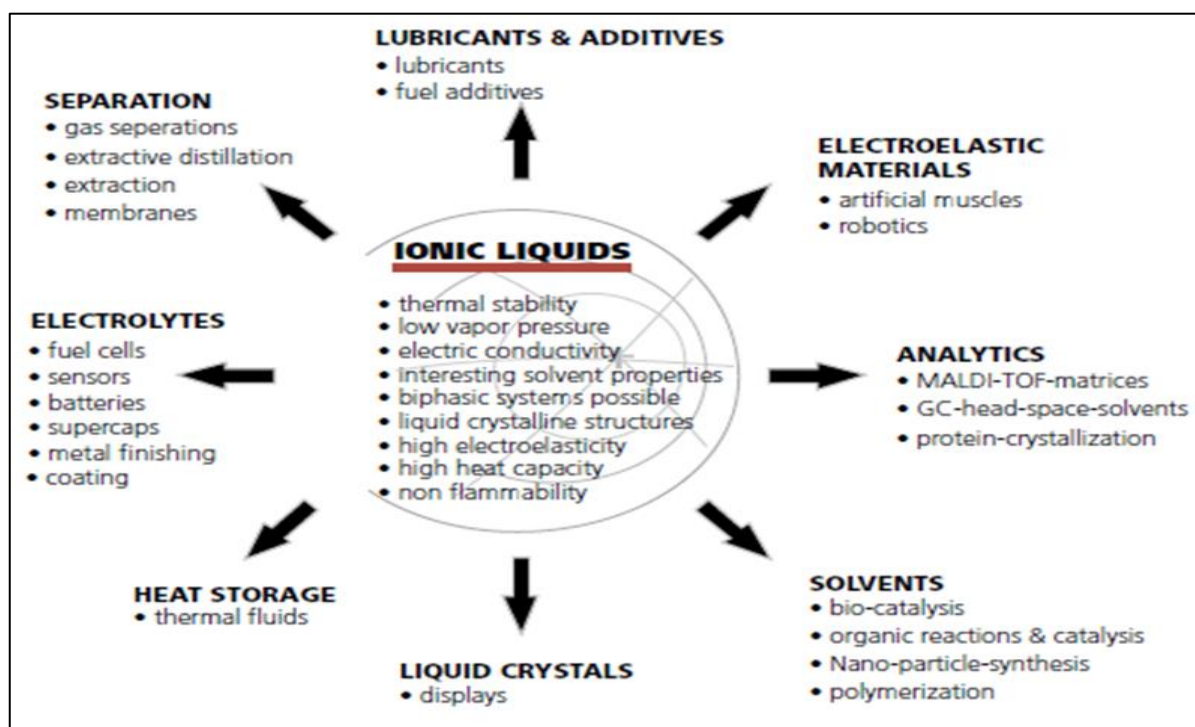


Figure 2-3: The important properties of Ionic Liquids (ILs) and their potential and current applications.

2.5 Experimental Work on Ionic Liquids

Kowsari et al., (2013) discussed about the effect of diesel fuel which is one of the largest sources of fine particle air pollution, that lead to serious health impacts. In the beginning of 2001, Environmental Protection Agency (EPA) passed the rules requiring use of ultra-low sulphur diesel (ULSD). The benefit from the usage of (ULSD) is it lowers the level of released sulphur and hydrocarbon to almost zero. Thus, the technology for reduction of sulphur in diesel fuel up to 15 part per million (ppm) which is currently available and the new technologies are under development that could reduce the cost of desulfurization. It also mentioned chemical oxidation in conjunction with ionic liquid extraction can increase the removal of sulphur sharply. Besides, ionic liquids have the ability of extracting aromatic sulphur compounds at ambient condition without consumption of hydrogen, H_2 . The cations, anions structure, and size of ionic liquids are important parameters affecting the extracting ability. In addition, ionic

liquids are immiscible with fuel, and the used ionic liquids can be regenerated and recycled by solvent washing or distillation process.

Valla et al., (2007) exhibit a research about the effect of heavy aromatic compounds on sulphur. There are five different model of sulphur compounds were studied, like benzothiophene, 2-methyl-benzothiophene, 3-decyl-thiophene, dibenzothiophene, and 4,6-dimethyl-dibenzothiophene. Each one of them was diluted in conventional gas oil in order to maintain a realistic hydrocarbon environment. After that, their cracking behaviour was studied using a steamed deactivated FCC catalyst, while the run tests were performed in an automated Short Contact Time Microactivity Test Unit (SCT-MAT). The result obtained at the end of the experiment showed the long chain alkyl-thiophene, 3-decyl-thiophene is mainly responsible for the increase of sulphur amount in diesel during cracking. That sulphur compound was also the most reactive one with respect to desulfurization, since it was highly cracked to H_2S and decomposed to S. The reactive order of the five heavy sulphur compounds during the FCC process is 3-decyl-thiophene > benzothiophene > dibenzothiophene > 4,6-dimethyl-dibenzothiophene > 2-methyl-benzothiophene.

Fox et al., (2010) prepared the experiment to enhance the desulfurization of model fuels using a film-shear reactor. The application of a film-shear reactor provides a remarkable enhancement in the efficiency of the ODS process compared to normal stirring. If the flow rate and all parameters were held constant, the extent of thiophene removal increased as the residence time increased. The results from the experiments showed that an increase in oxidant concentration did not lead to increased thiophene removal.

Zhao et al., (2009) prepared the desulfurization of fuel oil by pyridinium-based ionic liquids. The ionic liquid [BPy] BF_4 was found to be very effective for the extraction of sulphur components, thiophene and dibenzothiophene (DBT) in model oils and diesel at room temperature. The effects of extraction desulfurization on model oil with sulphur components were tested. The desulfurization process was achieved after H_2O_2 was utilized for oxidizing the sulphur components to the corresponding sulfones which were extracted by ionic liquid. The desulfurization of thiophene and DBT by the extraction-oxidation system can reach maximum value, 78.5% and 84.3% which are higher than those achieved by extractive desulfurization. The used ionic liquid was regenerated

through re-extraction in tetrachloromethane, and can be recycled four times without any obvious decrease in activity.

Wang et al., (2006) presented competitive extraction capacity of different ionic liquids for model fuel. The ionic liquids used for the experiment were based on FeCl_3 , ZnCl_2 , SnCl_2 , MnCl_2 , and lastly CoCl_2 . From the result obtained, the ionic liquids based on FeCl_3 showed the better extraction capacity of dibenzothiophene (DBT) from diesel than other ionic liquids. The sulphur removal of DBT-containing model oil can reach 67.6% with single extraction under mild condition while the extraction capacities for the other ionic liquids were below than 50.0%. The extraction process went on quickly, and it could reach extraction equilibrium in a short period. Furthermore, Fe-based ionic liquids system shows considerable promise for providing a technology to meet future needs for low sulphur diesel.

Zhang & Zhang (2002) presented selective sulphur removal from fuels by using ionic liquids at room temperature. In their work, three ionic liquids, [BMIM] $[\text{PF}_6]$, [BMIM] $[\text{BF}_4]$ and [EMIM] $[\text{BF}_4]$ were found to have distinctive absorption for sulphur containing compounds, allowing the removal of sulphur from fuels at room temperature. The model compounds used were 2-methylpentane, 1-hexane, methylcyclopentane, toluene, trimethylbenzene, thiophene, 2-methylthiophene, and isobutyl mercaptan to represent typical molecules in diesel fuels. The absorption capacity of an ionic liquid for a specified compound was measured at room temperature by the weight gain in the ionic liquid phase at saturated absorption. The ionic liquid [BMIM] $[\text{PF}_6]$ and [BMIM] $[\text{BF}_4]$ when applied to a mixture of thiophene and toluene showed there was stronger absorption for thiophene rather than toluene. For a specific aromatic compound such as thiophene [BMIM] $[\text{PF}_6]$ and [BMIM] $[\text{BF}_4]$ have higher absorption capacity than [EMIM] $[\text{BF}_4]$. It is because of the structure and the size of both cation and anion of ionic liquid that affect the absorption capacity. Besides, it was found that high level of aromatics does not significantly affect the absorption of ionic liquids for sulphur compounds.

Xuemei et al., (2008) presented the desulfurization of diesel fuel by extraction with $[\text{BF}_4]$ -based ionic liquids. The results show that the absorption capacity of an ionic liquid for the S-compound in diesel fuels relies on its structure and its size. In the case of the two examined diesel fuels, both elongating the cation tail length and increasing

the mass ratio of ionic liquid/ diesel fuel promote the desulfurization ability of the examined ionic liquids. Besides, the results show that imidazolium-based ionic liquids displays higher extraction efficiencies than pyridinium-based ionic liquids, presumably owing to the fact that the rings of the S-compounds are similar to the imidazolium head ring. The rates of the first desulfurization of diesel using [C₈mim] [BF₄] suggest that that ionic liquid is a promising extractant for desulfurization of the diesel fuels. The rate of desulfurization can reach up to 39.76%.

Wang et al., (2010) developed the extractive desulfurization of fuels using ionic liquids based on FeCl₃. Six Lewis acid ionic liquids were synthesized and employed as extractants for desulfurization of the model oil containing dibenzothiophene (DBT). The ionic liquids based on FeCl₃ showed the better extraction capacity than other based ionic liquids such as Zn, Sn, Mn and Co. At the end, it shows that 1-butyl-3-methylimidazolium chloride was very promising ionic liquid, which performed perfectly in the studied ionic liquids under the same operating conditions. It can remove DBT from model oil after continuous extraction for four steps, and the desulfurization efficiency can reach maximum value under mild reaction conditions. The used ionic liquid could be regenerated six times without a significant decrease in activity.

Dharaskar et al., (2009) prepared eleven Lewis acid based ionic liquids were screened to investigate the desulfurization efficiency. FeCl₃ based ionic liquid used as an effective extractant for removing DBT from liquid fuel. [BMIM]Cl/ FeCl₃ found to be the best ionic liquid as a kind of novel extractant for desulfurization of ionic liquid fuel, which exhibits a better extractive performance for DBT. The used ionic liquid, FeCl₃ was able to extract DBT from model liquid fuel even without regeneration. Furthermore, Fe based ionic liquids system shows considerable promise for providing a technology to meet future needs for low sulphur fuel or clean fuels.

3 MATERIALS AND METHODS

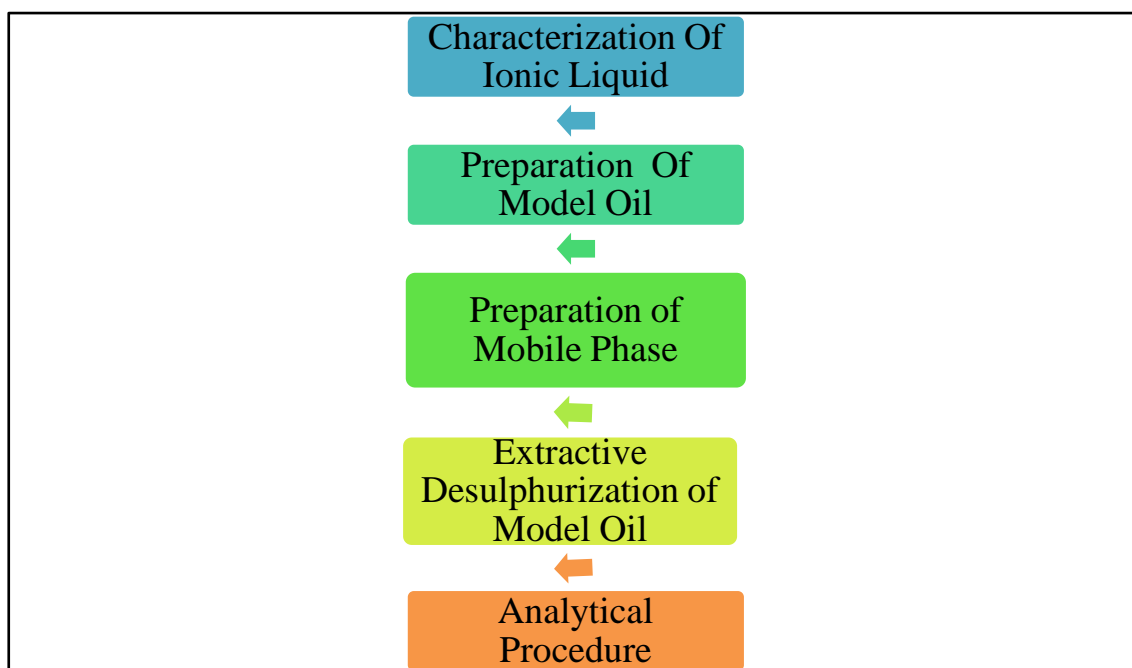
3.1 Overview

This paper presents the preparation to set up the experiment of desulfurization. The chemicals and the apparatus need during the experiment are listed down based on the procedures. The rare chemicals are usually not available in the laboratory, so those chemicals need to be purchased from the supplier. Besides, this chapter also focused on how the ionic liquids and model oil are being prepared in the laboratory. The procedure continue with the extraction on model oil, the ionic liquid is tested on the model oil first to observe the ability of its absorption capacity on DBT before tested it with diesel.

3.2 Chemicals & Apparatus

The materials involved in this experiment are DBT, 1-Methypyrazolium Methylsulphate, Methanol (standard for HPLC), water, Xylene and diesel needed to purchase from the supplier. The basic apparatus for this experiment such as beaker, test tube with rack, round bottomed flask, vials, Fourier transforms infrared spectroscopy (FTIR), (HPLC), magnetic stirrer, syringe, dropper, and others are obtained from the laboratory.

3.3 General methodology



3.4 Characterization of ionic liquid

The method for synthesis of ionic liquids was neglected because of several problems while purchasing the chemicals from outsiders. The chemicals needed were expected cannot be delivering on time. Thus, the initial ionic liquid was replaced with 1-Methylpyrazolium Methylsulphate. Then, the procedure was proceeding with characterization (CHNOS test) of new ionic liquid by sending it to UMP Central Lab and to determine the probability of its functional groups by Fourier transform infrared spectroscopy (FTIR) test.

3.4.1 Sample preparations

The (ILs) is obtained from Universiti Teknologi Petronas (UTP) via our course lecturer. The amount of (ILs) is very limited but enough for almost all of the usage in the experiments.

3.4.2 Fourier transforms infrared spectroscopy (FTIR)

This equipment is a measurement technique whereby spectra are collected based on measurements of the coherence of a radiative source, using time.

The ionic liquid, 1-Methylpyrazolium Methylsulphate was tested with a FTIR to check the functional groups. It is then followed by a wavelength classification by referring it to a table of characteristic IR absorptions (see Table 4-1). The procedure start with by placed the head of FTIR and connected to a host. Then, place a (Ge) plate. Approach the needle with the (Ge) plate and save the background spectrum. The liquid was placed on a Germanium (Ge) plate by using a dropper and the test is run until a constant reading is visible. For cleaning (Ge) plate purpose, a drop of acetone is used. From the classification, it was found that there is a trace of functional groups consists of amines, amides, aromatics and alkyl halides. The wavelength can be observed from the absorptions data.

3.4.3 Elemental analysis using CHNS

The ionic liquid was undergone a CHNOS testing to check the percentage of Carbon, Nitrogen, Oxygen and Sulphur that is present in the ionic liquid. The ionic liquid was sent to University Malaysia Pahang (UMP) Central Laboratory to obtain the results. The time duration was one week for the result before any other experiment can be conducted. From the data obtained, it was found out that there was presence of sulphur in the ionic liquid.

3.4.4 High Performance Liquid Chromatograph (HPLC) test

This equipment is a measurement technique to separate a mixture of compounds in analytical chemistry and biochemistry with the purposes of identifying of purifying the individual component mixture.

Before the High Performance Liquid Chromatography (HPLC) analysis can be done several steps will be prepared. Firstly, the ionic liquid that has been premixed with DBT and the model oil of xylene will be separated and put into a series of 5 vials. The vials are then going through an incubating shaker for 2 days at 180 rpm and at 30°C. After that, 1.5 L methanol obtained and filtered using a filter pump. It is then put under “degas” treatment for 30 minutes at 27°C and this will be the mobile phase for the HPLC analysis. Next, pure water is obtained in the laboratory. The analysis is conducted and set up under the guidance and supervision of the laboratory assistant. The result will be obtained and printed out and tabulated to be used in the discussion

part in the result section. From the results, a calibration curve based on the standard sample will be plotted and will be compared with the ionic liquid sample.

3.5 Preparation of model oil

For this investigation, a solution of sulphur compound, Dibenzothiophene (DBT) in xylene was employed as a model fuel.

0.06 mg of DBT was dissolved in 73 mL xylene to form 1421 ppm DBT content in the model oil. From 2000ppm DBT, it was diluted to 1421 ppm, 1000 ppm, 800 ppm, 500 ppm and 250 ppm of DBT. The sample was used to be analysed for standard calibration curve in this research.

Table 3-1: Concentration and Area for Standard Calibration Curve.

Concentration (ppm)	Area (mAU*s)
250	501.15227
500	299.59027
800	703.91636
1000	1327.12846
1421	3303.06999

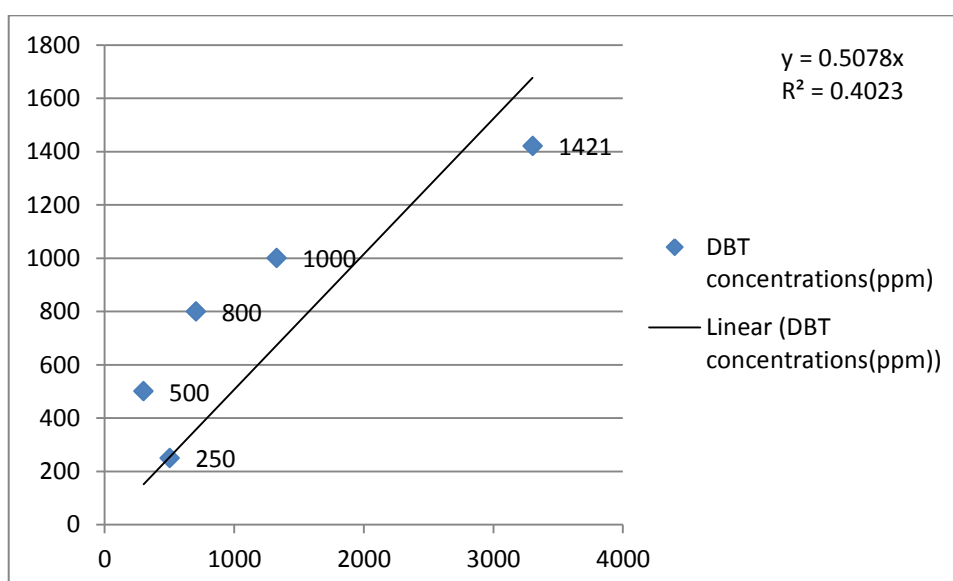


Figure 3-1: Area versus DBT Concentration.

3.6 Preparation of mobile phase

The selection of mobile phase is based on the desired retention behaviour and the physiochemical properties of the analyte. For this analysis, methanol and ultra-pure water as a mobile phase with ratio 90:10 (900 mL of methanol and 100 mL of ultra-pure water) was mixed in the scotch bottle. The mobile phase then was filtered with membrane-type filter with a porosity of 0.45 μ m to remove mechanical particle by pumping it using a vacuum pump. After all the mobile phase was already filtered, then the mobile phase was degassed by sonification to avoid the formation of bubbles in the detector cell.

3.7 Extractive desulphurization of model oil

The experiment was conducted by using model oil with 1421 ppm, 1000 ppm, 800 ppm, 500 ppm, and 250 ppm of DBT. The ionic liquid and model oil were mixed at 1:1 volume ratio which is 0.5 mL Of IL and 0.5 mL model oil in the universal bottle. The mixture in the bottle was heated in water bath at 30 °C with 185 rpm stirring for 30 minutes. The mixture then allowed settling for 5 to 10 minutes to obtain the splitting. After that, the sample from xylene layer was taken from the mixture by using needle syringe 6 mL. Before transfer the sample to the vial bottle, the needle was change by nylon filter. So that, the sample was filter before enter the 3 mL vial bottle. The procedures were repeated for different ionic liquids model oil mixing ratio (1:1).